

THE EFFECT OF FUEL SULFUR LEVEL ON THE HC, CO AND NOX CONVERSION EFFICIENCIES OF Pd/RH, Pt/RH, Pd-ONLY AND TRI-METAL CATALYSTS

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INTRODUCTION: Due to additional requirements imposed by the 1990 amendments to the Clean Air Act, automotive emissions systems must perform at high efficiencies for 100,000 miles⁽¹⁾. However, fuels containing sulfur, can reduce the efficiency of many modern catalyst formulations^(2,3). Additionally, the Northeast Ozone Transport Commission (OTC) has petitioned the U.S. Environmental Protection Agency (EPA) to require region-wide adaptation of the California Low-Emission Vehicle standards without the application of California's reformulated gasoline program⁽⁴⁾ which is necessary to keep the level of fuel sulfur low. As will be seen, this will result in reduced catalyst activity in the OTC, since typical gasolines contain sulfur levels which vary considerably. Gasolines containing 50ppmS and 500ppmS only represent the 10th and 75th percentile of U.S. commercial summer fuels⁽⁵⁾. As will be shown, these high levels of fuel sulfur will lower the performance of high activity catalyst formulations and may make compliance with LEV/ULEV emissions levels extremely difficult if not impossible without the adaptation of low-sulfur fuels.

EXPERIMENTAL: Dynamometer-based catalyst durability testing and evaluations were used to determine the effects of fuel sulfur levels on HC, CO and NOx conversion efficiencies of fully formulated Pd-only, Tri-Metal (Pt/Pd/Rh), Pt/Rh and Pd/Rh catalysts. These four catalyst technologies were evaluated at two degrees of catalyst aging (4K and 100K miles) using three fuel sulfur levels (34, 266 and 587 ppmS). For all testing, di-tert-butyl disulfide was used as the fuel-sulfur dopant. Test procedures included a series of equilibrium lightoff, transient lightoff and dynamic Air/Fuel ratio sweep experiments. These experiments were designed to reflect the most common operating conditions of a vehicle's emission system during typical driving. The lightoff experiments were designed to mimic the cold start process of the vehicle as the catalyst warms up. The dynamic A/F ratio experiment was designed to mirror the conditions which occur during feedback control of the engine at cruise. The slightly rich performance of the emissions system which occurs during mild transients can be assessed from the A/F ratio sweeps presented. The effects of fuel sulfur on all conditions are presented. To expose the catalysts to sulfur, 30min. of engine operation using a fuel with a prescribed sulfur level at an A/F ratio of 15.3 and a catalyst inlet gas temperature of 400°C was used.

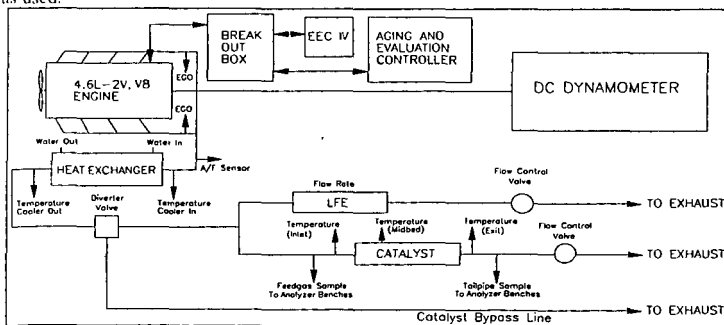


Figure 1: Schematic of engine test facility.

Experimental Hardware Exhaust gases from a 1993 Ford 4.6L 2V engine were routed through a heat exchanger into a test catalyst brick (see figure 1) for evaluation. The brick was located 2m downstream of the exhaust manifold flange. The inlet gas temperature to the catalyst was regulated by adjusting the load on the engine or by adjusting the amount of water flow through the heat exchanger. Correspondingly, the flow rate to the test catalyst was controlled by adjusting either the engine load or by diverting a fraction of the exhaust flow through a second flow path in parallel with the catalyst sample. The amount of diverted exhaust was measured by a laminar flow element (see Figure 1; LFE) in the secondary stream. To allow for transient lightoff experiments on each catalyst, a rapid switching valve was placed in the exhaust stream) to initially divert the exhaust flow around the test catalyst so the initial state of the catalyst could be set to ambient conditions. Continuous gas samples (one pre- and one post-catalyst) were withdrawn into two Horiba emissions benches and analyzed each second for CO, total HCs and NOx. A UEGO sensor and Air/Fuel Ratio Controller provided the necessary hardware to control the engine A/F ratio in a prescribed way.

Catalyst formulations, description and aging

Eight catalyst bricks of four different formulations were evaluated. One formulation was Pt/Pd/Rh (1/14/1); one was Pd-only (0/1/0); one was Pt/Rh (5/0/1); and the other was Pd/Rh (0/9/1). Their respective precious metal loadings were 105, 110, 60 and 40g/Ft². They were all fully formulated containing stabilizers, scavengers and base metal oxides. The Tri-metal and the Pd-only catalysts were of a two-layer washcoat design. In each layer, the particle sizes were optimized to promote higher catalyst efficiency when sulfur is added to the feedgas. They all contained 400 cell/in² and a cell wall thickness of 0.068in. They were all of

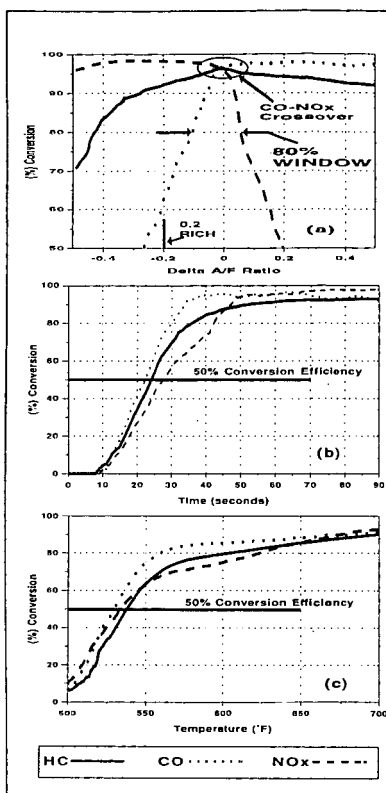


Figure 2: a) Sweep test; b) transient lightoff test; c) equilibrium lightoff test. Pd-only 4K.

thermally equilibrate during experimentation. This was accomplished by passing the engine exhaust through a water controlled heat exchanger, which regulated the temperature of gases entering the catalyst. As above, the engine was operated at steady state; its air flow rate was 30.3g/s; and its mean A/F ratio was 14.2. About this mean A/F ratio, the 1Hz, ± 0.5 A/F ratio modulation was applied. During the experiment, two gas samples were withdrawn continuously and analyzed every second for CO, total HCs and NOx. Corresponding catalyst conversion efficiencies ($(U_{\text{inlet}} - U_{\text{outlet}}) / U_{\text{inlet}} \times 100\%$) were determined as a function of inlet gas temperature into the catalyst. Figure 2b shows a typical catalyst equilibrium light-off trace for the 4K Pd-only catalyst. Clearly marked are the temperatures corresponding to 50% conversion of CO, HC and NOx. These values are used later to assess the early lightoff potential of catalyst formulations and the effects of sulfur poisoning on catalyst lightoff.

Transient Light-Off Test Description

To assess how a combination of substrate thermal inertia and the low-temperature catalyst chemistry affects the lightoff performance of the catalyst, the Transient Light-Off Test was conducted after cooling the catalyst brick to $38 \pm 2^\circ\text{C}$ to define the initial state of the catalyst. These conditions are typical of those which occur during the cold start of a vehicle. Here, the engine was operated at the same conditions used for the equilibrium lightoff experiments. Initially, gases from the engine bypassed the catalyst through a diverter valve while the engine was stabilized for the experiment. At the start of the transient lightoff experiment, the engine exhaust gas flow was suddenly switched into the flow path which contained the cold catalyst brick. Two gas samples were withdrawn continuously and analyzed every second for CO, total HCs and NOx, and the corresponding conversion efficiencies were determined as a function of time from the beginning of the warmup period of the catalyst. Figure 2c shows a typical transient light-off trace as conversion efficiency versus time, and marks the time necessary to attain 50% conversion of the inlet CO, HC and NOx. Prior to this time, mostly raw emissions pass the catalyst into the atmosphere and this "lightoff" time must be minimized/eliminated to attain LEV or ULEV emissions levels.

RESULTS and DISCUSSION: Typical vehicle operation includes cold start activation, warmed-up stoichiometric cruise, and slightly-rich accelerations with all modes present in the FTP-75⁽⁶⁾ driving schedule used to assess vehicle emissions performance. Over this cycle, a vehicle typically produces an engine-out emissions level of 1.3g/mi THC, 10-12g/mi CO, and 1.5-3.0g/mi NOx. These emissions are then converted at high efficiency over the catalyst system to more environmentally acceptable chemical species. To attain 100K ULEV emissions levels (0.055/2.1/0.3g/mi;

the same dimension (3.15"x4.75"x6.00") and total volume (76in³). Preceding experimentation, four catalysts were dynamometer aged to the equivalent of 4K miles and four to 100K miles of vehicle use. During this procedure, a commercial unleaded gasoline which contained 160ppmS was used.

A/F Sweep Test Description

The A/F sweep test was conducted by operating the engine at a steady state air-flow of 30.3g/s while ramping the fuel flow rate from a lean to rich A/F ratio. This ramp consisted of the superposition of linear and sinusoidal components. The linear component ranged from +1.0 to -1.0 A/F ratios about stoichiometry and occurred over 360s. The sinusoidal component had an amplitude of 0.5 A/F; its frequency was 1 Hz. It was used to evoke all active kinetics over the catalyst including the O₂ storage mechanism. For all experiments, the A/F ratio sweep started at an A/F ratio of 15.2 (A/F_{stoich} = 14.2 for California Reformulated Fuel) and proceeded to an A/F ratio of 13.2. The inlet gas temperature at the catalyst was $450 \pm 5^\circ\text{C}$ and the space velocity (at STP) into the 76in³ catalytic monolith was 85,000 Hr⁻¹. Figure 2a shows a typical result of a sweep test. The abscissa represents $\Delta A/F$ ratio (i.e., $A/F_{\text{Actual}} - A/F_{\text{Stoich}}$). The ordinate shows the CO, HC and NOx conversion efficiencies, the CO-NOx crossover efficiency, and the A/F ratio operational window. Values are also marked at a slightly rich A/F ratio, since these values are used later to show the effects of sulfur level on fuel-rich catalyst performance. These results are critical in determining the "best" catalyst performance for a vehicle operating under warmed up conditions and mild accelerations.

Equilibrium Light-Off Test Description

The equilibrium light-off test was performed to assess how the low-temperature chemistry over the catalyst evolves without the complications associated with transient substrate warmup. It was conducted by "slowly" ($12.3^\circ\text{C}/\text{min}$) increasing the inlet gas temperature to the catalyst, thus allowing the catalyst substrate to

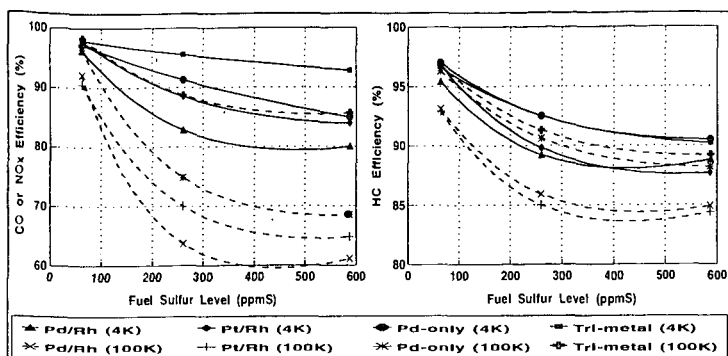


Figure 3: a) CO and NOx conversion efficiency at the A/F ratio corresponding to CO/NOx crossover during sweep testing; b) HC conversion efficiency at CO/NOx crossover. Solid curves represent 4K aged catalysts; dashed curves 100K catalysts.

HC/CO/NOx), average emission system efficiencies of greater than 97%, 81% and 86% are necessary. However, these averages assume that the emissions system is operational and functioning at high efficiency from key-on of the vehicle. Generally, the vehicle and emissions system start cold and the catalyst requires time to warm to its lightoff temperature, hence passing unconverted emissions to the atmosphere. Since CO and HC emissions are abundant during cold start, the average CO and HC efficiencies over the remainder of the drive cycle must be significantly higher than the averages specified above. As seen in figure 3, when sulfur level is low, these high efficiencies are obtained for Pd-only and Tri-metal catalysts and would also be obtained for Pu/Rh and Pd/Rh with more catalyst volume in the emissions system. However, at higher levels of fuel sulfur and at 100K aging, all efficiencies drop well below the levels needed to attain LEV and ULEV. As seen later, catalyst lightoff is also negatively impacted by fuel sulfur, thus further exacerbating the problem.

Warned Up Catalyst Operation. Figure 3 presents the catalyst efficiencies at the A/F ratio corresponding to the CO/NOx crossover point (see Fig 2) and figure 4 shows them at an A/F ratio of 14.0. These A/F ratios are chosen since they reflect many of the typical operating points of a warmed up vehicle that occur during cruise and mild accelerations. Since three way catalysts must simultaneously convert HC, CO and NOx at high efficiency, the CO/NOx cross over point is normally near the A/F ratio corresponding to optimum catalyst operation. As seen in figure 3a, the CO/NOx efficiencies of all catalyst formulations are greater than 96% efficient at low sulfur levels and at low mileage. Moreover, when aged to the equivalent of 100K miles, these formulations have conversion efficiencies in excess of 92% when low sulfur levels are present in the fuel. Here, the efficiencies of the Tri-metal and the Pd-only are in excess of 96.5% after 100K aging, and the efficiencies of the Pu/Rh and the Pd/Rh formulations are 91% and 92%, respectively. However, for 100K aged catalysts, when sulfur is added to the fuel during evaluation, the CO/NOx efficiencies of these catalysts drop. For the Tri-metal (the most resistant to sulfur poisoning due to its multi-layer structure and advanced stabilizers), the efficiency falls from 98% to 86% when the fuel sulfur level goes from 34 to 587 ppmS; Pd-only from 96% to 69%; Pu/Rh from 92% to 65%; and the Pd/Rh from 92% to 65%. At 4K, the ordering of sensitivity to sulfur poisoning is similar to the above at 100K aging with the amount of lost performance being less. In terms of the change in emissions throughput ($(1.0 - \%Eff/100)_{LowS} / (1.0 - \%Eff/100)_{HighS}$), the effect of changing fuel sulfur level from 34 to 587 ppmS would increase the amount of CO and NOx delivered to the atmosphere by approximately 4-9 times the amount delivered when the fuel sulfur level is low. As seen for the 100K catalysts, much of this lost performance occurs when the fuel sulfur level increased from 34 to 267 ppmS with the catalysts becoming less sensitive to the addition of sulfur above these levels.

The effect of sulfur on HC conversion efficiencies is shown in figure 3b. Trends are similar to those discussed above. However, since HC conversion efficiency must be extremely high to meet LEV or ULEV emissions regulations, the level of efficiency loss due to the addition of sulfur to the fuel will make it extremely difficult or potentially impossible to reach these low emissions levels with the most advanced catalyst formulation developed to date. As seen in figure 3, near stoichiometry the Pd-only catalyst ranks first behind the Tri-metal in efficiency throughout the range of sulfur application. Even though it is susceptible to sulfur²³, its higher initial activity at low sulfur is retained throughout the range of typical sulfur application when operated near stoichiometry. Its performance is higher than that of the Pu/Rh or Pd/Rh catalysts studied. As mentioned, this is in part due to its higher initial activity and in part due to the combination of materials which comprise its washcoat to reduce its sensitivity to sulfur. Here, the catalyst is of a multi-layer design containing an abundance of ceria and lanthana plus scavengers to inhibit the detrimental effects of sulfur. Furthermore, the particle sizing in each layer has been optimized to enhance reaction at high sulfur level.

Results of catalyst performance at an average fuel-rich A/F ratio of 14.0 (0.2 rich of stoichiometry and oscillating at 1Hz) are shown in figure 4. Here, HC, CO and NOx efficiencies are presented for 4K and 100K aged catalysts as fuel sulfur level is increased from 34 to 567 ppmS. As seen, the performance of all catalysts is substantially reduced when sulfur is added to the fuel. As an example, when the sulfur level is low, the NOx conversion efficiency for all catalyst formulations is greater than 95% for both 4K and 100K aged catalysts. Here, the Tri-metal formulation shows the least

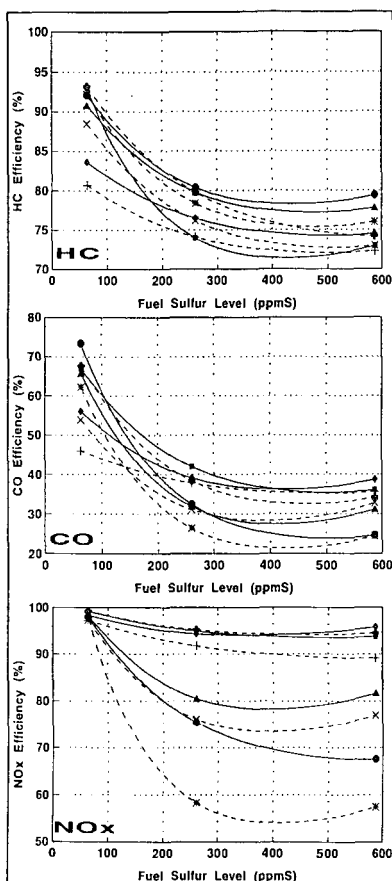


Figure 4: HC, CO and NOx efficiency versus sulfur level. Solid curves indicate 4K aged catalysts; dashed curves indicate 100K aged catalysts. Note: See figure 3 for legend.

metal catalyst has a multi-layered washcoat, the Pd-containing layer in this structure promotes low temperature lightoff. At higher sulfur levels, the lightoff temperature for the Pd-only and the tri-metal formulations continue to be lower than the Pt/Rh and the Pd/Rh catalysts due to their higher initial activities and the incorporation of stabilizers and scavengers into their formulations to resist sulfur poisoning. At 100K and high sulfur levels, both the tri-metal and the Pd-only formulations have the lowest lightoff temperature.

Upon reproducible vehicle cold start, a direct relationship should exist between catalyst lightoff temperature, lightoff time and cold start emissions, assuming the catalysts have identical substrate thermal inertia, and heat and mass transfer characteristics. Here, transient lightoff experiments were conducted to assess the lightoff time of each formulation, at all sulfur levels and at 4K and 100K. Figure 6 shows the results of these transient lightoff experiments. The curve shows the relationship between lightoff time for our experimental geometry and catalyst lightoff temperature. It should be noted that the exact values of lightoff time are unique to these experimental conditions. Both mass flow rate and inlet gas temperature profile are critical to the absolute values of lightoff time. As expected, as the lightoff temperature increases, the lightoff time increases. Since all catalyst bricks were of the same geometry, containing the same thermal inertia and geometric surface area, the only major difference between formulations arises through their differences in critical lightoff temperature. As seen, there is a direct linear correspondence between lightoff temperature and lightoff time for all catalysts studied. This suggests that the catalyst which retain the lowest lightoff temperatures during aging and poisoning will lightoff sooner during vehicle cold start, thus producing fewer cold start emissions. As seen in the figures 5 and 6, increased sulfur concentration increases lightoff temperature for all catalysts, suggesting that the corresponding vehicle emissions will be impacted in a negative manner.

sensitivity to sulfur having its NOx efficiency drop from 98% to 95% for both 4K and 100K of aging. The order of NOx efficiency loss under rich operating conditions among all catalyst formulations goes from Tri-metal to Pt/Rh, to Pd/Rh and to Pd-only. The Tri-metal being the least sensitive and the Pd-only being the most sensitive as sulfur is added to the fuel.

Generally, to meet LEV and ULEV emissions levels, NOx conversion efficiencies around 90% are necessary at 100K miles. As seen in figure 4, when sulfur level is low, all advanced catalyst formulations have an efficiency well above this value. However, when sulfur is added, the NOx conversion efficiency of both the Pd/Rh and the Pd-only drop below the levels needed to attain LEV or ULEV emissions levels. Moreover, with the possible addition of a high-speed, high-acceleration driving cycle to the test procedures, meeting the NOx standard with a high sulfur level in the fuel becomes even more difficult.

Catalyst Lightoff Experiments. In addition to the emissions generated during continuous operation, more than 80% of the CO and HC emission occurs during cold start of the vehicle before the catalyst becomes active. Any increase in "lightoff" temperature or "lightoff" time due to sulfur addition will present major problems in meeting LEV and ULEV emissions levels, since the exiting flux of HCs and CO are high during this period. Lightoff temperature corresponds to the temperature of the substrate at which the conversion efficiency of CO, HC or NOx reaches 50%. Lightoff time refers to the time during the transient test procedure at which the conversion efficiency of CO, HC or NOx reaches 50% conversion. Figure 5 shows the effect of added fuel sulfur on catalyst lightoff temperature of CO for all formulations studied. Lightoff temperature of HC and NOx will follow the same trends as of CO, since they are strongly dependent on the heat generated by the exotherm during CO lightoff.

In figure 5, the lightoff temperature is plotted as a function of sulfur level for each catalyst formulation. The tri-metal and the Pd-only catalysts have the lowest lightoff temperatures of all formulations at 4K and 100K aging. At low sulfur level, the lightoff temperature for the Pd-only and tri-metal catalysts are about 35°F lower than for the Pt/Rh and Pd/Rh catalysts. This is due to the excellent low temperature CO and HC kinetic properties of Pd. Since the tri-

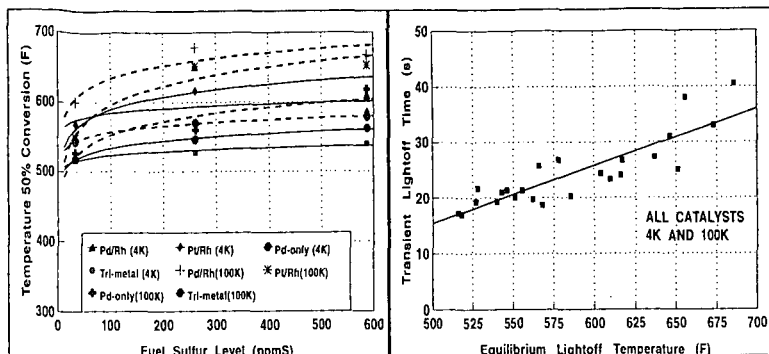


Figure 5: Lightoff temperature for CO: Solid Figure 6: Transient lightoff time versus lightoff temperature for all catalysts.

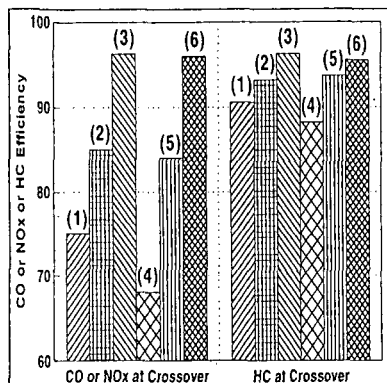


Figure 7: Conversion efficiency at CO/NOx crossover. Pd-only catalyst. Data at: 1) exp=260, eval=260; 2) exp=260, eval=34; 3) exp=34, eval=34; 4) exp=587, eval=587; 5) exp=587, eval=34; 6) exp=34, eval=34 ppmS.

Pd/Rh catalysts at 4K or 100K miles of aging during the application of 34, 260 or 587 ppmS to the fuel stock, results indicate that the application of sulfur reduces catalyst efficiency (the Tri-metal being the least affected) near stoichiometry and rich of stoichiometry. Moreover, it increases the lightoff temperature and the lightoff time of all formulations evaluated. The consequence of these results is the suggestion that, when operated on fuel containing elevated sulfur levels, overall vehicle emissions system performance will degrade due to the increased sulfur level. Fortunately, when fuel sulfur is removed much of the lost efficiency is regained, but to fully regain lost efficiency, a high temperature, rich cleaning process must be applied. As seen, conversion efficiencies for CO, HC and NOx necessary to achieve LEV or ULEV emission levels will be significantly lowered due to fuel sulfur and can impede attainment of these levels.

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Catalyst cleaning To assess the regeneration of the catalyst after exposure to sulfur, catalyst performance for all formulations was evaluated at several stages of cleansing. These stages included: 1) exposure at 260ppmS; evaluation at 260ppmS; 2) evaluation at 34ppmS; 3) evaluation at 34ppmS after high-temperature (660°C), rich (A/F=13.6) cleaning for 30min; 4) exposure at 587ppmS, evaluation at 587ppmS; 5) evaluation at 34ppmS; 6) evaluation at 34ppmS after high temperature, rich cleaning for 30 min. As seen in figure 6 for a Pd-only catalyst at the CO-NOx crossover point, more than half of the efficiency loss due to sulfur poisoning is regained when evaluation proceeded using a low-sulfur fuel. However, to regain nearly all efficiency loss, a rich high temperature cleansing of the catalyst was necessary and is in agreement with the work of Beck⁽²⁾ et al. In addition, trends for lightoff temperature are similar to these in that the application of sulfur in fuel raises the lightoff temperature and time of the catalyst and a high temperature cleansing is necessary to return it to its pre-exposure levels.

CONCLUDING REMARKS: In evaluating fully formulated Tri-metal, Pd-only, Pt/Rh and